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Quantitative analysis and spatial and temporal distribution of volatile organic compounds in atmospheric air by utilizing drone with miniaturized samplers

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ABSTRACT

Our second generation air sampling drone system, allowing the simultaneous use of four solid phase microextraction (SPME) Arrow and four in-tube extraction (ITEX) units, was employed for collection of atmospheric air samples at different spatial and temporal dimensions. SPME Arrow coated with two types of materials and ITEX with 10% polyacrylonitrile as sorbent were used to give a more comprehensive chemical characterization of the collected air samples. Before field sampling, miniaturized samplers went through quality control and assurance in terms of reproducibility (RSD $\leq$14.1%, N = 4), equilibrium time ($\geq$10 min), breakthrough volume (1.8 L) and storage time (up to 48 h). 128 air samples were collected under optimal sampling conditions from July to September 2019 at the SMEAR II station and Qvidja farm, Finland. 347 VOCs were identified in the air samples either on-site or in the laboratory by thermal desorption gas chromatography - mass spectrometry, and they were quantified/semiquantified using Partial Least Squares Regression models. Individual models were developed for the different coatings and packing materials using gas phase standards obtained by an automatic permeation system. Average gas phase VOC concentrations ranged from 0.1 (toluene, the SMEAR II station) to 680 ng L^{-1} (acetone, Qvidja farm). Average VOC concentrations in aerosols ranged from 0.1 (1,4-cyclohexadiene, the SMEAR II station) to 2287 ng L^{-1} (megastigma-4,6,8-triene, Qvidja farm). Clear differences in results were seen for samples collected at the SMEAR II station and Qvidja farm, between VOC compositions in gas phase and aerosols, and between the sampling site and height.

1. Introduction

The reliable identification and quantitation of volatile organic compounds (VOCs) in air is gaining an increasing interest in the scientific community and among the public authorities due to their responsibility of the air quality and human wellbeing (Melymuk et al., 2014). The simplest and most conventional way to quantify VOCs in air involve their direct measurement by sensors and mass spectrometers (Majchrzak et al., 2018; Mirzaei et al., 2016). However, the complex mixtures of compounds present in the air, most of them at low concentrations, require analytical approaches that allow the preconcentration of the target analytes during sampling followed by their subsequent individual isolation and detection. The employment of proper sampling technique, including efficient material, plays an important role in the successful separation and detection with high sensitivity (Lan et al., 2020).

Miniaturized air sampling (MAS) techniques are replacing the traditional air sampling strategies, e.g. sorbent packed traps and sorbent coated disks, by having several advantages, such as small size, low sampling time, easy operation, automation etc. (Lan et al., 2020). They also provide acceptable sensitivity, robustness, and flexibility for practical applications. In general, MAS techniques are mainly based on microextraction devices that can be divided into passive and active samplers. The first ones allow the sampling of gas phase compounds with almost negligible particle matter loading. The main challenge of these samplers for air analysis is the accurate quantitation of the target

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analytes. In most cases, variations in ambient sampling conditions, such as temperature, humidity and wind speed clearly affect their uptake rate (Lan et al., 2020). The active samplers allow the simultaneous collection of gas and particle phase compounds. Quantitative results can be easily achieved because most of the problems related to the variations of ambient sampling conditions can be avoided (Forbes, 2020). Usually only the evaluation of breakthrough volume is needed to ensure quantitative results.

Commercially available and widely used MAS techniques include solid phase microextraction (SPME) in various formats (fiber, arrow, thin-film, etc.) and sorbent packed needles and tubes, e.g. needle-trap device (NTD) and in-tube extraction (ITEX) (Lan et al., 2020). In our previous studies, SPME Arrow and ITEX systems proved to be useful MAS techniques (Feijó Barreira et al., 2018; Lan et al., 2019a; Ruiz-Jimenez et al., 2019). SPME Arrow unit, as an alternative to SPME fiber, has a redesigned structure with increased physical stability and improved capacity by having stainless steel substrate and larger volume coating. ITEX is a miniaturized active sampler that enables collection of a large volume of sampled air and result in a high sensitivity to the trace airborne VOCs. Most of the commercially available MAS systems can be operated in manual or automatic mode, but SPME Arrow is the most commonly used in on-site analysis due to its simplicity and portability (Lan et al., 2019a; Ruiz-Jimenez et al., 2019).

The use of aerial drones as carrier for different sampling systems has become a very popular alternative to conventional air sampling platforms at high altitudes such as airships, aircrafts, tethered balloons and meteorological towers (Chen and Pawliszyn, 2004). The versatility, flexibility and easy operation of drone based systems allow the almost simultaneous sampling at different heights and positions even in places that are difficult to access (McKinney et al., 2019). The optional use of different accessories, attached to the active sampling systems, avoid potential interferences such as moisture, ozone, or particles (Ruiz-Jimenez et al., 2019). In addition, the use of electronic engines with propellers minimizes the potential contamination during the sampling (Chang et al., 2016). However, aerial drone carriers have also some clear limitations related to the payload weight capacity, flight time, battery endurance etc. Benefits of the MAS systems, such as the short sampling time and the low total weight, might partially overcome these problems (Lan et al., 2020). However, the effect of air pressure and velocity under the drone on the MAS should be evaluated (Villa et al., 2016).

The simultaneous use of active and passive MAS systems in combination with a drone sampling platform allows the clarification of the VOCs distribution between gas phase and particles. The SPME fibers combined with NTD have been successfully applied to the evaluation of the particle/gas phase distribution in the case of pesticides (Niri et al., 2009), terpenes (Reyes-Garcés et al., 2013) and pheromones (Eom et al., 2012). In addition, ITEX and SPME Arrow units have been employed in a drone sampling platform for atmospheric air collection in the remote forest and wetland (Ruiz-Jimenez et al., 2019).

Different problems, related to the reliability of the identification and quantitation of a large number of compounds, have been detected for the determination of VOC profiles in air. Most of them are observed for non-targeted analysis of environmental and biological samples. The use of strict and well documented criteria during data processing has allowed the reliable verification of the identified compounds avoiding incorrect results even in the absence of standards and reference materials (Kopperi et al., 2013). Up to 53 VOCs were identified during the winter time in the atmospheric air in the southern Finland (Ruiz-Jimenez et al., 2019).

It is well known that the quantitation of the identified compounds is a challenging task. In addition to the typical issues belonging to the development of calibration curves for a passive/active sampling technique (Pawliszyn, 2011), the lack of individual standards for all the identified compounds should be pointed out. Then calibration curves can be developed for active and passive sampling systems using different approaches, such as permeation system, sample vials containing gas phase standards, liquid injection and liquid standard addition on sorbent bed (Pawliszyn, 2011; Ruiz-Jimenez et al., 2020). Each of these options has their own advantages and drawbacks, but when compared with each other, the permeation system provides the most reliable results for the determination of VOCs in air samples, including very volatile compounds (Ruiz-Jimenez et al., 2020).

In all cases, standard chemical compounds are needed for the development of the calibration curves. Surrogate approaches are often exploited when calibration standards are not available for all identified compounds. A high prediction error for concentrations calculated with the surrogate approach can be reduced by implementing multiple surrogates and their mass spectral similarities in partial least squared regression (PLSR) models. This approach has been previously employed for environmental samples resulting in good prediction accuracies for the concentrations of unknown compounds (Kopperi et al., 2013, 2016).

In this study, a reliable method for quantitative/semi-quantitative gas chromatography – mass spectrometry (GC-MS) analysis of hundreds of VOCs in air using drone with miniaturized samplers was developed. Prior to on-site sampling, the quality assurance and quality control of the miniaturized samplers, in terms of reproducibility, repeatability, breakthrough volume, equilibrium time, and storage time, were performed in the laboratory. The effect of propellers on the passive and active air sampling was evaluated on-site. The composition of different fractions of the air as gas phase (SPME Arrow sampling) and aerosol particles (ITEX sampling) was evaluated at different heights and locations in two sampling sites (the SMEAR II station and Qvidja farm) during July–September 2019. Individual identified VOCs were successfully quantified/semi-quantified based on the PLSR models obtained from the calibration curves of 23 standard compounds including organic oxygen compounds, lipid-like molecules, carbonyl compounds, alcohols, organonitrogen compounds, benzene and its substituted derivatives, ketones, aldehydes and prenol lipids.

2. Experimental

2.1. Reagents and materials

Detailed information of materials and reagents is found in the supplement (S1).

2.2. Permeation system

The permeation system used in this study is the same as in our previous work (Ruiz-Jimenez et al., 2020). Detailed description can be found in the supplement (S2).

2.3. Quality assurance and quality control

Before field sampling, several experiments were conducted sequentially in the laboratory to evaluate the reliability of the procedures using MAS. These experiments were based on the use of the permeation system, described in the previous section, containing 9 VOC compounds (trimethylamine (TMA), triethylamine (TEA), methyl isobutyl ketone (MIBK), hexanal, alpha-pinene, *p*-cymene, 3-carene, acetophenone, and nonanal) as model compounds. Prior to sampling, the SPME Arrow and ITEX systems were spiked with internal standard (ISTD) using 1 min extraction and 5 mL of ISTD vapor.

The sampling kinetics of polydimethylsiloxane-divinylbenzene (PDMS/DVB)- and mobil composition of matter No. 41 (MCM-41)-SPME Arrows were evaluated with 8 different sampling times between 2 and 30 min using triplicates. Sampling times over 30 min were not tested due to the maximum 30 min flying time of the drone with a single battery.

The breakthrough flow rate and volume were evaluated for 10% polyacrylonitrile (PAN)-ITEX that was selected due to its good extraction capacity to most of the airborne VOCs, high permeability, and good

thermal stability. According to our previous studies, the flow rate should not exceed ~60 mL min^{-1} if a 30 min sampling is required (Lan et al., 2019a). At the same time, the loss of pre-added ISTD can be avoided. Therefore, the breakthrough volume was –retested for the compounds under study using 8 different sampling times, ranging from 1 to 30 min in triplicate with a flow rate of ~56 mL min^{-1}.

Reproducibility of the packing and coating procedures was evaluated for four units of PAN-ITEX, PDMS/DVB-SPME Arrow, and MCM-41-SPME Arrow using triplicate measurements for each of them. The sampling time was 30 min.

Finally, the storage time of air samples in SPME Arrow and ITEX was tested as follow: standards were collected with the different samplers for 30 min and analyzed immediately as the control, referred to a 100% recovery. Samplings were repeated and the SPME Arrow and ITEX were stored at −20 °C in the freezer for 24 and 48 h before analysis. The compound losses were evaluated by calculating the ratio between the stored sample and the control sample.

2.4. Configuration of the sampling systems in drone

A remote-controlled Geodrone X4L (Videodrone, Finland), dimensions of 58 × 58 × 37 cm (width × depth × height) and a total weight of 2 kg, was used as the air sampling platform. The setup in the drone was similar as in our previous study (Ruiz-Jimenez et al., 2019) with some modifications (Fig. 1) that can be found in supplement S3.

2.5. Sampling sites and sample collection

2.5.1. Sampling sites

One of the sampling sites was the SMEAR II Station (Station for Measuring Ecosystem-Atmosphere Relations II), a flagship station for atmospheric research located in a Scots pine forest in Hyytiälä, southern Finland (Lan et al., 2019b; Ruiz-Jimenez et al., 2019). Two sampling locations at the SMEAR II Station were selected. One was beside a fixed sampling tower surrounded by forest (61°50′46.93″N, 24°17′43.04″E) and the other one was at the lakeshore (61°50′44.12″N, 24°17′2.40″E).

Another sampling site was the Qvidja farm (60°17′42.30″N, 22°23′32.70″E), located in Parainen, Finland (https://www.qvidja.fi). Qvidja farm, consisting of 140 ha of field surrounded by 650 ha of forest. It is considered an important basement for agricultural and environmental research beside farming. Among other activities it should be emphasized the creation of a space for biodiversity in and above ground, the development of emissions-free energy production sources, and the use of effective renewable energy storage methods, sequester carbon in soil, and recycle nutrients. The plants in the field included timothy (*Phleum pratense*), rye-grasses (*Lolium*), common meadow-grass (*Poa pratensis*), and red fescue (*Festuca rubra*). The animal species are also diverse, including cows, sheep and horses. Four sampling locations were used at Qvidja farm and these are shown in Fig. S1.

2.5.2. Sampling at the SMEAR II station

The influence of propellers, sampling height and location on the VOCs profiles of the gas and aerosol phases was investigated from the 1st to 12th of July 2019 at the SMEAR II station. The effect of the propellers was evaluated next to the sampling tower, used as reference, and both locations (sampling tower and lakeshore) were used for the evaluation of the effect of the sampling height and location to the results. PDMS/DVB-SPME Arrow and 10% PAN-ITEX sampling systems were used for these experiments, and they were spiked with ISTD prior to air sampling using the permeation system for ISTD described in supplement S2. The samples collected by SPME Arrow and ITEX were analyzed on-site with the manual thermal desorption unit (MTDU) and gas chromatography-mass spectrometry (Lan, 2019; Ruiz-Jimenez et al., 2019). Effect of the propellers on the MAS, as a function of the relative position between the propellers and the samplers, was evaluated in a single experiment. The drone box, the drone leg and under the propeller, a 1-m long wooden stick was connected to the drone legs allowing the sampling under the propeller, were evaluated in the case of the SPME Arrow. Just the drone leg and under the propeller were evaluated in the case of ITEX. The sampling time of 15 min and sampling height of 18 m were used. Reference samples, not affected by propellers, were collected from sampling tower in parallel to the drone flights. The tower was ~10 m away from the sampling location of the drone and the samples were collected at the same height than the samples collected using the drone.

In order to quantitatively analyze the VOCs in the atmospheric gas and particle phases, sampling was performed once a day during four days in the forest and the lakeshore. An approach similar to our previous study was used for the sampling height replacement (Ruiz-Jimenez et al., 2019). The sampling heights were 5 m and 50 m for 30 min. Alternating 5 min samplings at these two heights were successively carried out to simulate the simultaneous sampling at two heights. A quick battery change (ITEX pump off and SPME Arrow close) was needed after 30 min to complete the total 1 h sampling time. Two SPME Arrows and two ITEXs were used at each height.

2.5.3. Sampling at Qvidja farm

During each day in the Qvidja farm (from the 23rd of July to 10th of September 2019), air sampling was performed sequentially at four different sampling locations, defined as A, B, C, and D (Fig. S1). 30 min sampling was made at both flying heights 50 m and 150 m. The sampling height was changed in the same way as in Hyytiälä. 10% PAN-ITEX and PDMS/DVB-SPME Arrow sampling systems were used for collecting air at 50 m and another 10% PAN-ITEX system together with MCM-41-SPME Arrow were collecting air at 150 m. The ISTD was always

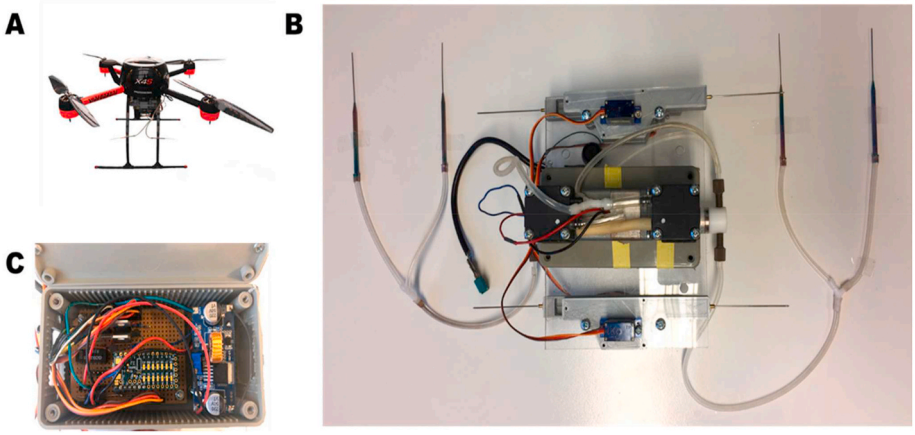

Fig. 1. Aerial drone as a carrier for miniaturized air sampling systems. A) Air sampling platform. B) Sampling box details. C) Sampling box controller electronics.

spiked (sampled) in the laboratory before air sampling. After air collection, the sampling systems were stored at −20 °C and carried to the laboratory for analysis. Storage time was less than 24 h before GC-MS analysis. 150 m is the maximum sampling height accepted without any permission by the Finnish law for civil unmanned aerial vehicle flying.

2.6. Instruments and GC-MS analysis

Detailed information about instruments and GC-MS analysis is found in supplement (S4).

2.7. Data handling and statistical analysis

Raw data were converted to the open format mzML, using MassHunter Qualitative 8.0, prior to data processing. An ADAP-GC (Automated Data Analysis Pipeline) based MZmine 2 (version 2.53) workflow was developed to detect, deconvolute and align the chromatographic peaks (Fig. S2) (Pluskal et al., 2010; Smirnov et al., 2018). Peaks found on the zero samples (conditioned SPME Arrows and ITEXs) were removed from the data before identification of the aligned peaks. The identification of these peaks was developed by manual comparison of their mass spectra and retention indices with NIST2014 database. The final criteria for tentative identification of VOCs involves a spectral match >800 and ± 100 as the maximum difference between experimental and library Kováts indices.

Different R, version 3.6.3, tools were used in this research for statistical analysis (Team, 2019). Quantitation of the tentatively identified VOCs was carried out by a previously described PLSR approach with some modifications (Kopperi et al., 2013, 2016). Firstly, calibration curves of 23 compounds were obtained by a permeation system with ≥5 different concentrations, which covered at least two order of magnitudes. Then, these 23 VOCs were distributed into 9 groups according to their taxonomical classification (Table S1) (Djoumbou Feunang et al., 2016). Quantitative determination of VOCs was carried out by PLSR. Response factor for each compound was calculated using the ratio between the peak area of the analyte and the ISTD. In each group, the response factors derived from the peaks in total ion chromatograms were then converted to ion intensities on the basis of relative abundances of individual ions in their mass spectra (RF_i (m/z)) (Kopperi et al., 2013). The equations developed for the different groups of compounds, sampling technique and materials were subsequently validated according to statistical parameters.

Linear discriminant analysis (LDA), a supervised pattern recognition approach, was used to establish differences between the different samples collected during the field sampling based on their chemical composition. The concentration of the different VOCs (expressed as ng L^{-1}) was used as input variables in all the cases.

3. Results and discussion

3.1. Quality control and quality assurance of the MAS-drone system

The selection of SPME Arrow coating materials was based on the exceptional selectivity of MCM-41 for small aliphatic amines and the capability of PDMS/DVB to collect less volatile and aromatic compounds (Lan et al., 2019b; Ruiz-Jimenez et al., 2019). 10% PAN-ITEX sampling system was selected due to its excellent permeability for air flow, acceptable thermal stability, and high affinity to a wide range of VOCs (Lan et al., 2019a).

SPME Arrow, as a passive air sampler, captures the gaseous compounds from the air based on their partial distribution between the gas phase and the sorbent. SPME Arrow air sampling can be an equilibrium approach (Feijó Barreira et al., 2018; Pawliszyn, 2011) or a non-equilibrium approach (Chen et al., 2003; Chen and Pawliszyn, 2004; Martos and Pawliszyn, 1997). Among them, the former is more practical and less prone to errors when the sampling time is close to the equilibrium time. The equilibrium time of PDMS/-DVB- and MCM-41-SPME Arrow for 9 representative compounds (listed in section 2.3) was firstly tested (Fig. 2A). Most of the compounds did not reach equilibrium in PDMS/DVB-SPME system within 30 min due to the large pore size and volume of DVB particles (Lan et al., 2019b). Only hexanal, MIBK, and TMA reached equilibrium at 15–30 min due to their relatively low affinity to the sorbent phase compared to other compounds. Due to much smaller pore size (~4 nm) (Lan et al., 2019b), MCM-41-SPME Arrow system reached equilibrium for nonpolar monoterpenes (alpha--pinene, *p*-cymene, and delta-3-carene) within 10 min. Because it has higher affinity to small polar compounds, e.g. TMA, TEA, MIBK, hexanal, acetophenone, and nonanal, equilibrium for these needed more than 30 min.

In order to achieve quantitative results with ITEX, suitable air flow rate and sampling time need to be known. In our previous study, three template compounds were retained in 10% PAN-ITEX system with a flow rate of ~60 mL min^{-1} for 30 min (Lan et al., 2019a). ISTD retained also for more than 1 h without breakthrough. Here, the sampling time was retested with other template compounds. There was no breakthrough within a half hour sampling for many of the compounds under study at the flow rate of 60 mL min^{-1} (Fig. 2B). However, breakthrough was reached for TMA, TEA, 3-carene and *p*-cymene in 20–25 min.

In order to study the spatial and temporal distribution of VOCs in the atmospheric air, the variations between different SPME Arrow or ITEX sampling systems were evaluated to compare the results and to ensure their reproducibility. Three types of air samplers, PDMS/DVB-SPME Arrow, MCM-41-SPME Arrow, and 10%PAN-ITEX, used for on-site sampling, were tested in terms of reproducibility. Commercial PDMS/DVB-SPME Arrow exhibited the best reproducibility between four devices and the average relative standard deviation (RSD) of 9 compounds in terms of their peak area was 4.0%. MCM-41-SPME Arrow (N = 4) and 10%PAN-ITEX (N = 4) systems gave also good reproducibility with the average RSD of 14.1% and 9.6%, respectively. All the data were feasible, allowing the reliable comparison between different SPME Arrow and ITEX systems.

The samplers, used in this study, needed to be stored for a period of time before analysis. At the SMEAR II station, the storage was less than 2 h since the samples were analyzed on-site. The samples collected at Qvidja farm were taken to the laboratory for analysis in 24 h. Therefore, the storage conditions for the samplers were evaluated in order to know the possible losses or decomposition of the analytes during the storage. As can be seen from Fig. 2C, no losses or analyte decomposition occurred during 48 h, meaning that −20 °C was a practical storage temperature for our applications.

It is well known that drone propellers cause airflow disturbance during the flight, affecting the concentration of gas phase and aerosol particles in the air surrounding the drone. To minimize their effect, many authors have analyzed the airflow to determine the optimum installation positions of the sensors and/or the sampling lines (Li et al., 2020; Villa et al., 2016). The very high-quality facilities available at the SMEAR II station allowed in this study the evaluation of the exact location of the active and passive sampling systems in the drone by comparing the results obtained by simultaneous sample collection by three SPME Arrow (DVB-PDMS) and two ITEXs (10% PAN) systems positioned as described in section 2.5.2 with the reference values, obtained for the samples collected using the same systems at the sampling tower located 10 m away from the drone sampling position. The sampling time of 15 min and height of 18 m were selected to provide representative results for subsequent analysis of natural samples. In addition, the selection of the sampling height was related to the availability of sampling places in the tower. These experiments were done in triplicate.

Results achieved for evaluation of the effect of the propellers on the results can be found in Table S2. The number of compounds identified in the different samples ranged from 55 to 60 for SPME Arrow system and

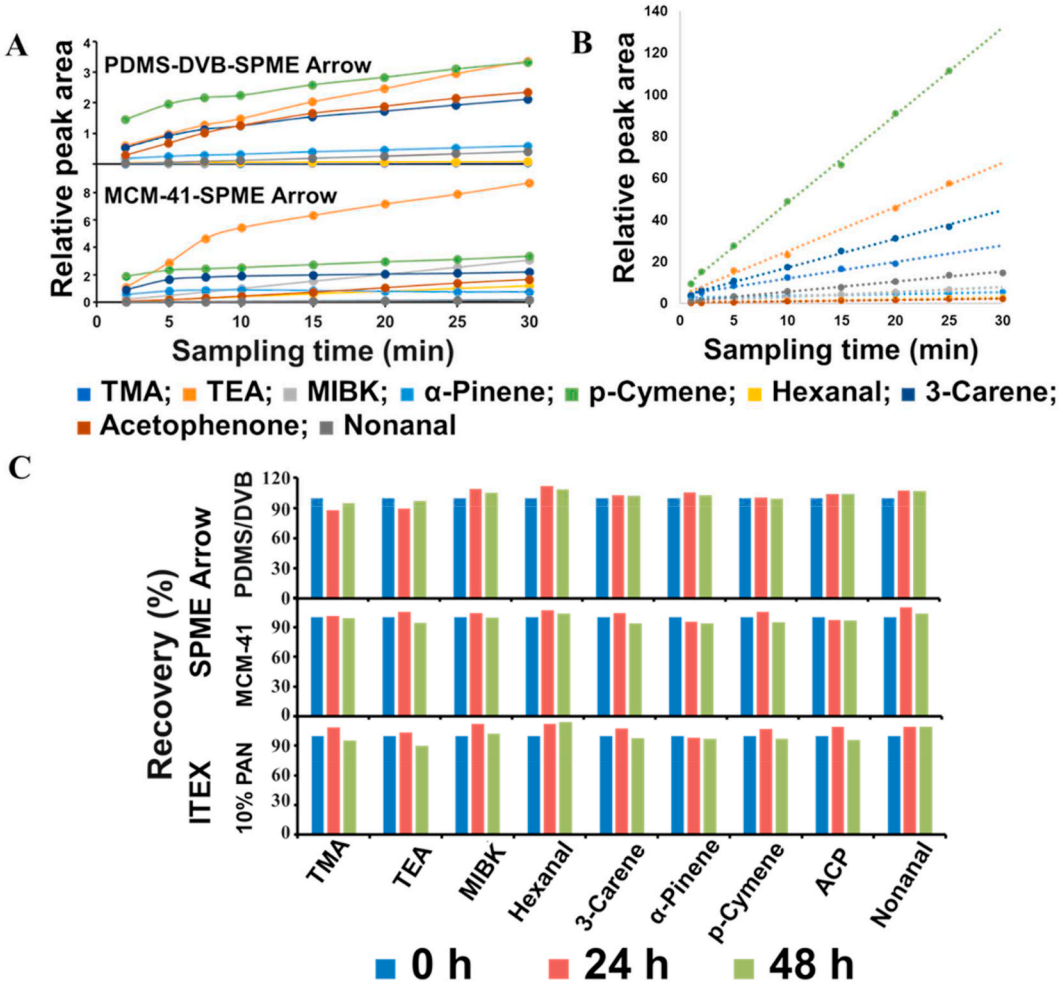

Fig. 2. Quality control and quality assurance of the SPME Arrow and ITEX samplers. A) Effect of the sampling time on SPME Arrow recovery. B) Effect of the sampling time on recovery with 10% PAN-ITEX system. C) Effect of storage time on recovery (%) with SPME Arrow and ITEX sampling systems. ITEX flow rate was 60 mL min^{-1}. The Y axis is the relative peak area of analytes (relative to ISTD).

from 62 to 73 for ITEX system. The effect of the propellers on the SPME Arrow (passive sampler) system depended of the relative position between the sampler and the propeller, giving in all the cases smaller mean recoveries when compared to those obtained in the reference sampling place. These values ranged between 90.8 and 98.2% for the SPME Arrow system placed in the sampling box. However, major differences were found for the samples collected at the two other positions. Recovery values ranged from 65.6 to 74.2% and from 78.0 to 86.9% for the SPME Arrow located in the leg of the drone and under the propeller, respectively. No significant effect of the drone propellers on the ITEX system (active sampler) was observed in this study, extraction recoveries ranged from 99.7 to 103.7% for all the different positions under study.

The results obtained confirmed that the selection MAS position on the drone platform is fundamental to minimize the effect of the drone propellers on the results during sampling (especially with SPME Arrow passive samplers).

3.2. Development of partial least squares regression equations

The criteria for the selection of the following compounds 2-butanol, 2-ethyl-hexanol, 1-octanol, 1-propanol, hexanal, nonanal, octanal, pentanal, toluene, ethyl-benzene, o-xylene, 3-methylbenzylamine, MIBK, acetophenone, 2-butanone, acetone, D-limonene, 3-carene, *p*-cymene, α-pinene, TEA, pyridine and TMA for model compounds for the development of the PLSR equations were following: (1) All of them have been detected in outdoor air samples using MAS techniques (Lan et al., 2019a, 2019b; Ruiz-Jimenez et al., 2019). (2) Potential reactions between model compounds must be avoided on the permeation system. For this reason, carboxylic and dicarboxylic acids were not included as model compounds. However, these compounds were quantified using other carbonyl compounds as surrogates. In addition, amines were not mixed with alcohols or carbonyl compounds during the calibration procedures to avoid potential reactions between standards. Decafluorobiphenyl was selected as ISTD due to its relatively high volatility, good chromatographic properties and potential absence in the natural air samples. Moreover these model compounds were distributed into groups according to their taxonomical classification, resulting in the formation of 9 different compound groups (Djoumbou Feunang et al., 2016), such as organic oxygen compounds, lipid-like molecules, carbonyl compounds, alcohols, organonitrogen compounds, benzene and its substituted derivatives, ketones, aldehydes and prenol lipids, containing at least 4 compounds per group (Table S1).

Partial least squares regression equations were developed for the different compound groups, sampling techniques and coating/packing materials using the procedures and approaches described in our previous manuscript (Kopperi et al., 2013). A total number of 27 PLSR equations were developed using the response factor vectors (RF (m/z)), calculated as a function of the mass spectra provided by the instrument, as explanatory variables. The real concentrations of the different model compounds, expressed as ng L^{-1}, were used as response variables. The

number of the RF (m/z) used for the development of the different equations, the mean concentration value and the standard deviation are summarized in Table S3. Standard laboratory error (SEL), associated with preparation of the gas phase standards, was 20 pg L^{-1}. Since the standard deviation of the samples used for the development of the PLSR equation was higher than SEL, the theoretical R^2 for the PLSR equation was 0.99 according to the Mark and Workman criterion (Mark, 1991; Mark and Workman, 1987).

Before the equation development, the datasets were divided into calibration and validation sets, containing 75 and 25% of the RF (m/z), respectively. Table S3 summarizes the final number of RF (m/z) vectors used for the development of the equations, the optimal number of PLS factors, R^2 prediction values and standard error cross-validation (SECV) for the different PLSR equations used in this study. The criterion proposed by Shenk and Westerhaus (Shenk et al., 1996), based on the R^2 values and SECV, allowed evaluation of the different equations. The values provided by the equation for R^2 prediction indicated excellent precision in all the cases.

The applicability of the model for the quantitation of those compounds not included in the model (external compounds), was evaluated by a procedure similar to cross-validation (Workman and Springsteen, 1998). Table S4 lists the final number of RF (m/z) used in the development of the validation equations, their optimal number of PLS factors, the R^2 values, the SECV and the prediction errors (EPE). The mean values for the prediction errors ranged from 15.3% to 26.1% for prenol lipids (10% PAN-ITEX sampling) and benzene and its substituted derivatives (DVB/PDMS-SPME Arrow sampling), respectively. These values were considered equivalent to the prediction error of the main PLSR equation for the external analytes (EPE).

Finally Table S5 summarizes detection and quantitation limits obtained for the different compounds used for the development of the equations. These values are closely related to the LOD and LOQ provided by the PLSR models considering that the signals used as variables for the development of the equations are taken from the chromatograms.

3.3. Qualitative and quantitative analysis of airborne VOCs

Peaks in the chromatograms were detected, deconvoluted, aligned and identified as described in the experimental section. Once identified, the individual VOCs were classified according to their taxonomical group and quantified/semi quantified using the PLSR equations developed in the previous section. The simultaneous use of passive and active sampling systems enabled the determination of VOCs both in gas and particle phases. The passive samplers gave directly gaseous concentrations, but the VOC concentrations in particles were obtained by concentration differences between ITEX and SPME Arrow samplers. The use of different PLSR equations for the calculation of the concentrations as a function of the sampling technique and material minimized the potential differences caused by the sampling technique. Finally, visualization of a large amount of data might be problematic. Individual concentrations of the compounds belonging to the same taxonomical group were summed up within the same sample in order to fix this problem. In addition, average concentrations were calculated for comparison studies.

3.3.1. Comparison of the samples collected at the SMEAR II station and Qvidja farm

Up to 346 VOCs were identified and quantified in the samples collected at the SMEAR II station and Qvidja farm during the summer 2019. The distribution of these compounds between the different sampling sites is clear. Less than 10% of the compounds were found in both SMEAR II and Qvidja samples, no matter whether the samples concern gas phase or aerosol particles (Fig. S3).

The evaluation of the VOCs concentrations, calculated for the different taxonomical groups present in gas phase and aerosol particles, revealed also clear differences between the sites. In most of the cases, the highest VOC concentrations were observed for the samples collected at Qvidja farm with some exceptions, as seen in Fig. S3. Ketones showed the largest differences among gas phase compounds, and organonitrogen compounds and lipid-like molecules in aerosol particles. Detailed information about the individual VOCs present in the samples collected at both sites is given in the following sections.

Finally, the statistical influence of gas phase and aerosol particles composition on the differentiation between the SMEAR II station and Qvidja farm samples was evaluated using LDA. The composition of VOCs in gas phase and particles in 46 samples was used for the development of the classification model (36 for training and 10 for validation). The resulting model allowed the correct classification of 90% of the samples used for the validation, confirming the statistical influence of the VOCs composition, gas phase and aerosol particles, on the differentiation of the samples collected during the different sites.

The observed differences between the sites were larger than expected, most probably due to their clear differences. The SMEAR II station is located in a Scots pine forest with natural vegetation and animals, and the vegetation and animals of Qvidja farm are diverse, including natural and artificially planted vegetation, cows, sheep and horses. In addition, the weather conditions were very different between the sites. There were unusually low temperatures and a high number of raining days during SMEAR II sampling, and sunny days and summer temperatures during sampling at Qvidja farm. The changes in the meteorological conditions might affect the emissions/formation of gas phase compounds and particles. Finally, the different sampling parameters between the sites most probably affected the results as well. The SMEAR II samples were collected at the height of 5 and 50 m due to adverse weather conditions, while Qvidja farm samples were collected at the height of 50 and 150 m. Further evaluation for both sites is needed in the future considering all these potential sources of variation.

3.3.2. Comparison of gas phase and aerosol particle composition

The comparison of the gas phase and the aerosol particles composition for the samples collected at the SMEAR II station and Qvidja farm revealed that in both locations the number of compounds identified and the sum of their concentrations were larger in the aerosol particles than in the gas phase. The detailed analysis of the distribution of these compounds between gas phase and particles (Fig. 3) showed that the number of VOCs simultaneously detected in the gas phase and aerosol particles was over 63.9% in both locations. In addition, the number of compounds detected just in the gas phase was under 11% in all the cases. The relatively high number of compounds found only in particles (31.6% and 21.0% for the SMEAR II station and Qvidja farm, respectively) can be explained by adsorption process and different chemical reactions produced during the particle formation and growth.

The evaluation of the quantitative results by taxonomical groups (Fig. 3), for the samples collected at the SMEAR II station, demonstrated that VOC concentration in the aerosol particles was larger than in gas phase for all the taxonomical groups, with the exception of ketones and aldehydes. The opposite trend, higher concentration values in aerosol particles than in gas phase, was found for Qvidja farm samples with two exceptions, lipid-like molecules and organonitrogen compounds. The differences in the behavior of the samples collected at the different locations can be explained by the clear differences between the location of the SMEAR II station and Qvidja farm and those of sampling conditions described in the previous section.

As can be seen from Tables S6 and S7, 1,4 cyclohexadiene gave the highest concentrations from all the VOCs quantified in the aerosol particles and collected at the SMEAR II station, and megastigma-4,6,8-triene at Qvidja farm. Dimethylamine, ethylamine and organonitrogen compounds belonged also to major VOCs in the particles collected at Qvidja farm, and acetone with the highest concentrations in gas phase samples collected both at the SMEAR II and Qvidja sites.

The statistical significance of the differences observed for the VOC composition of gas phase and aerosol particles was evaluated using LDA. Two different LDA models, one per each sampling site, were developed

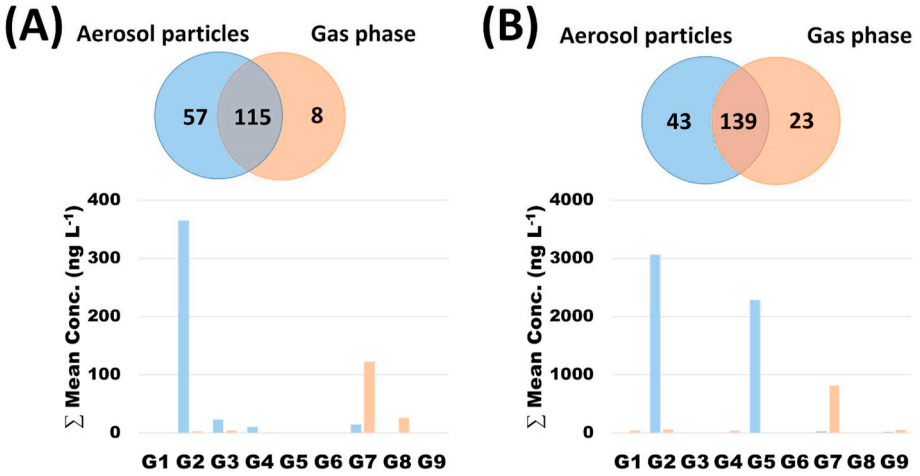

Fig. 3. Comparison between gas phase and aerosol particle composition for samples collected at the SMEAR II station (A) and Qvidja farm (B). The number of quantified compounds were plotted in Venn diagrams. G1, Organic oxygen compounds; G2, lipid-like molecules; G3, carbonyl compounds; G4, alcohols; G5, organonitrogen compounds; G6, benzene and its substituted derivates; G7, ketones; G8, aldehydes; and G9, prenol lipids.

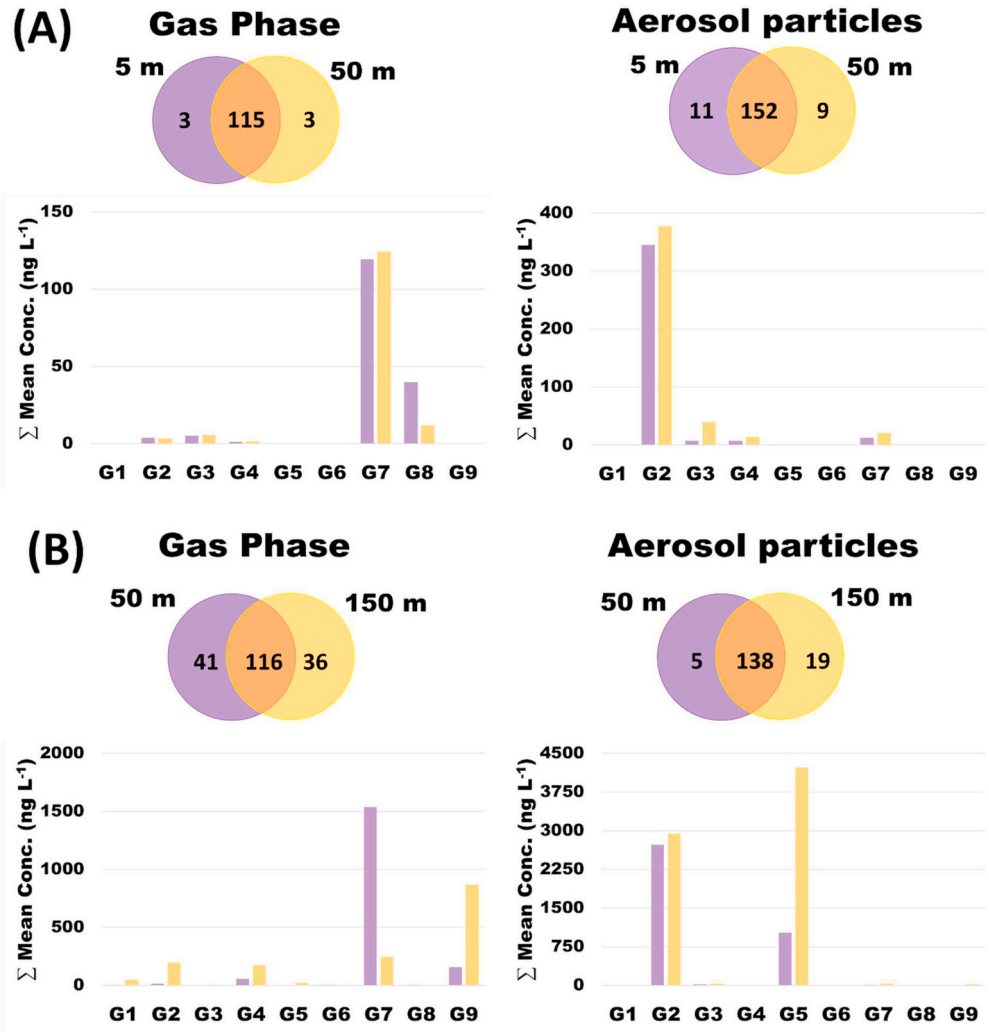

Fig. 4. Variation of the gas phase and aerosol particle composition with the sampling height for samples collected at the SMEAR II station (A) and Qvidja farm (B). The number of quantified compounds were plotted in Venn diagrams. G1, Organic oxygen compounds; G2, lipid-like molecules; G3, carbonyl compounds; G4, alcohols; G5, organonitrogen compounds; G6, benzene and its substituted derivates; G7, ketones; G8, aldehydes; and G9, prenol lipids.

due to large variations in the composition of the samples collected at the SMEAR II station and Qvidja farm. In this way, the VOC profiles of 29 samples (23 for training and 6 for validation) collected at the SMEAR II station and 64 samples (51 for training and 13 for validation) collected at Qvidja farm were used for the development of LDA models. Resulting models allowed the correct classification of 83.3% of the samples used for model validation of SMEAR II samples and 84.6% of Qvidja samples. The results confirmed the statistical differences in the composition of the analyzed samples. Detailed information of the taxonomical groups allowing the differentiation between samples can be found in Table S8.

3.3.3. Variation of the gas phase and aerosol particles composition with the sampling height

The influence of the sampling height on the VOC composition of the gas phase and the aerosol particles collected at the SMEAR II station and Qvidja farm was evaluated by sampling at two different heights in each site. At the SMEAR II station, samples were collected at 5 and 50 m. However, in the case of Qvidja farm, sampling was made at 50 and 150 m. The reasons for the selection of different heights for the collection of the samples were described in the previous section. In this way, results obtained from SMEAR II and Qvidja sites were processed in parallel.

As can be seen from Fig. 4, only minor differences, in the terms of number of compounds, were observed for the samples collected at different heights in the case of the SMEAR II station. Most of the compounds were simultaneously detected at both at heights in gas phase and aerosol particles. The same trend was observed for the aerosol particles collected at Qvidja farm. However, clear differences, in terms of number of compounds, were found for gas phase samples. In this case, just 59.1% of VOCs were found at both sampling heights.

To clarify the potential effect of the sampling height on the concentration of the gas phase and aerosol particle compounds, mean concentration values were calculated for the individual compounds determined for the samples collected at the different heights, with independent of the sampling location (Tables S9 and S10). An increase of the total VOCs concentration values with the sampling height was observed in the case of aerosol particles collected at both sampling sites. This increase was more relevant in the case of the samples collected at Qvidja site. Nitrogenated compounds were the responsible of the main differences in these samples (Fig. 4). In addition, lipid-like molecules and carbonyl compounds provided the largest differences between samples in the case of SMEAR II site (Fig. 4). These variations can be explained by an increase in the total number of particles with the height at relative low altitudes or a transport processes.

The total concentration of the gas phase compounds decreased with the sampling height at both sampling sites (Tables S9 and S10) and the detailed analysis of the results revealed that this trend is followed only by aldehydes for samples collected at the SMEAR II station and ketones for Qvidja farm samples (Fig. 4). In both sampling sites, the decrease in aldehyde and ketone concentrations with the sampling height was larger than the total increase of the other compounds (Fig. 4). These variations might indicate vertical mixing processes. Unfortunately, this study did not allow to make robust conclusion due to the low number of heights evaluated and their variation for samples collected at different sites.

The statistical influence of the VOC composition on the differentiation between samples collected at different heights was evaluated using LDA. 14 samples were used for the development of the LDA models for the SMEAR II station and 31 samples for Qvidja farm. All the SMEAR II samples were used for the model training, and 25 Qvidja farm samples for model training and 6 for validation. In both cases, developed models allowed the correct classification of 100% of the tested samples. Detailed information of the taxonomical groups allowing the differentiation between samples can be found from Table S11.

Finally, the evaluation of the concentrations of the individual VOCs present in the samples showed that acetone was once again the most abundant compound at both heights in SMEAR II gas phase samples (Table S9). It was found also at the highest concentration in the samples collected at height of 50 m at Qvidja farm. However, limonene was the most abundant compound at 150 m (Table S10). In addition, acetone was responsible for the largest differences between gas phase samples collected in Qvidja site at different heights. In the case of the SMEAR II station, the largest differences between gaseous samples at different heights were found for glyceraldehyde. 1,4-Cyclohexadiene was the most abundant compound at both sampling heights in SMEAR II aerosol particles, while megastigma-4,6(Z),8(Z)-triene was the most abundant in Qvidja farm particles (Tables S9 and S10). 1-Methyl-1,3-cyclopentadiene showed the largest concentration differences between aerosol particles collected at different height at the SMEAR II station and ethylamine at Qvidja farm.

3.3.4. Influence of the sampling location on gas phase and aerosol particles composition

The potential effect of the sampling location on VOC composition of gas phase and aerosol particles was evaluated for samples collected at the SMEAR II station from two sampling locations, one in the forest and another on the lake. At Qvidja farm, four different sampling locations (Fig. S1) were selected. To simplify the data analysis, the potential effect of the sampling height on the gas phase and aerosol particle composition was not considered in this study. Mean concentration values were calculated for the individual compounds determined in the samples collected at the different locations, with independent of the sampling height (Tables S12 and S13).

The evaluation of the results, in terms of number of compounds, obtained for the samples collected at the SMEAR II station (Fig. 5) showed that the number of VOCs in gas phase and aerosol particles were about the same at both sampling locations, most probably due to their similar emission sources. Largest differences were found for samples collected at Qvidja farm. A high number of potential emission sources and the presence of mixing and transport processes can explain this. In addition, the total number of compounds determined at the SMEAR II station in gas phase samples was smaller than that in aerosol particles. The opposite trend was found for samples collected at Qvidja (Fig. 5).

The evaluation, in terms of total VOCs concentration of the gas phase samples, sampled at the SMEAR II station gave the highest concentrations for the samples collected in the lake site. However, the opposite trend was observed for the aerosol particles (Table S12). In the case of the samples collected at Qvidja farm, the highest values for total VOC concentration were achieved for both gas phase and aerosol particles in the samples collected at place C. In addition, the highest and the lowest ratios between the total VOC concentrations in particles and gas phase were achieved for the samples collected at places D (3.5) and B (1.5), respectively (Table S13).

In terms of taxonomical groups, the results obtained at the SMEAR II station showed that at both sampling locations, ketones gave the highest concentrations in gas phase and lipid-like molecules in aerosol particles. In the case of the samples collected at Qvidja farm, ketones were the most abundant compounds in the gas phase in all the sampling sites. In addition, relatively high amounts of prenol lipids were present also in the case of gaseous samples collected at locations B and C. Different trends were observed for the aerosol particles. Lipid-like molecules provided the highest concentration values for sampling locations A and D. Nitrogenated compounds provided the highest concentration values for the samples collected at location B. Finally, both lipid-like molecules and nitrogenated compounds were present almost at the same concentrations at location C (Fig. 5).

The evaluation of the individual concentrations for the VOCs present in the samples proved again that acetone was the most abundant compound at both sampling places for gas phase samples at the SMEAR II station (Table S12). At Qvidja farm, acetone gave also the highest concentrations in the gas phase samples collected at sampling locations A, C and D. However, 1-hydroxy-2 propanone was the.

The statistical influence of the VOC composition on the differentiation of the samples collected at different locations was evaluated using

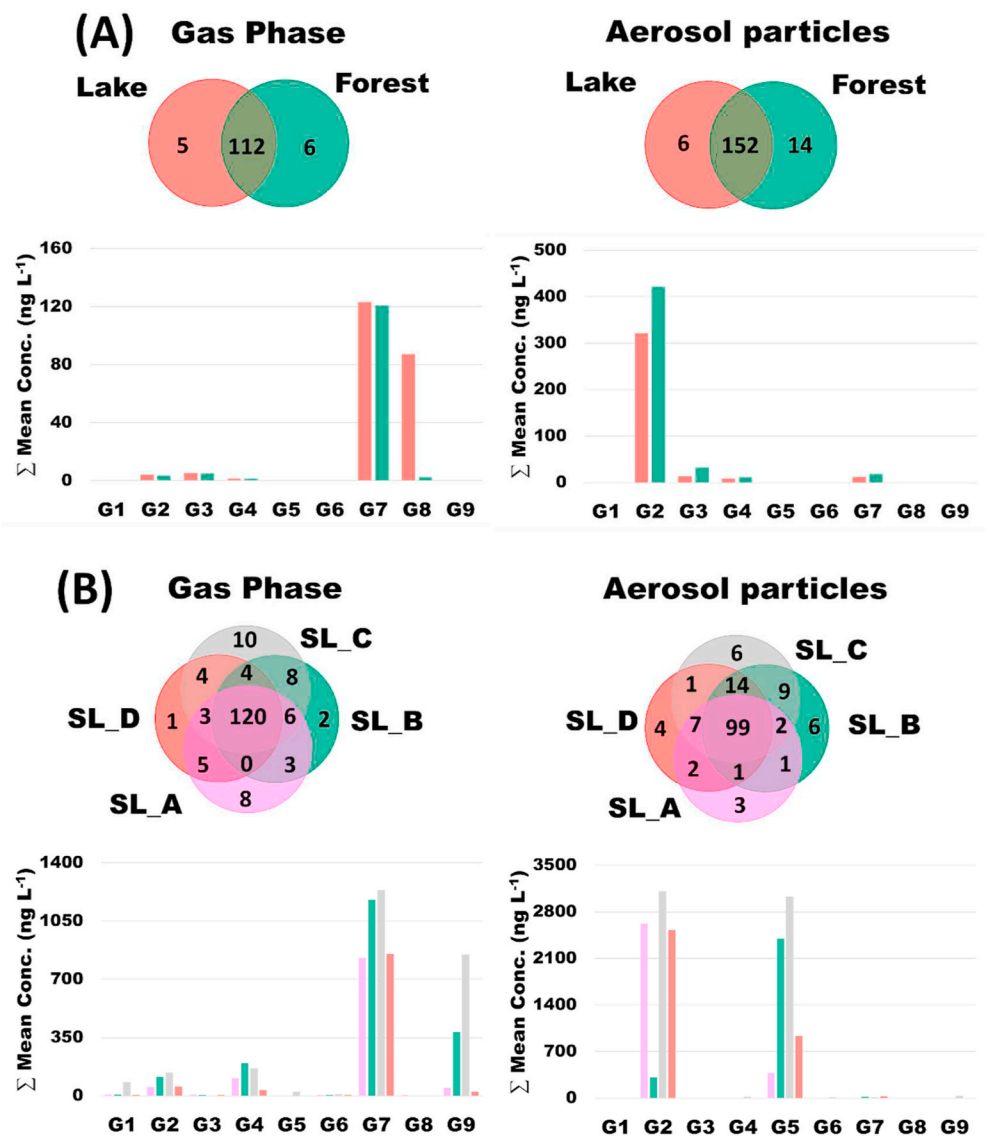

Fig. 5. Influence of the sampling location on gas phase and aerosol particle composition for samples collected at the SMEAR II station (A) and Qvidja farm (B). SL_A-D, sampling locations at Qvidja farm (additional information can be found on Figure S1). The number of quantified compounds were plotted in Venn diagrams. G1, Organic oxygen compounds; G2, lipid-like molecules; G3, carbonyl compounds; G4, alcohols; G5, organonitrogen compounds; G6, benzene and its substituted derivates; G7, ketones; G8, aldehydes; and G9, prenol lipids most abundant compound at location B (Table S13). 1,4-cyclohexadiene was the most abundant compound in the aerosol particles at both sampling locations at SMEAR II station (Table S12). At Qvidja farm, megastigma-4,6(Z),8(Z)-triene was the most abundant compound at sampling sites A, C and D, and dimethylamine had the highest concentrations at site B. (Table S13).

LDA. VOC composition in 14 samples, including gas phase and aerosol particles and collected at the SMEAR II station was used for LDA model development. The limited number of samples hindered to use training and validation sets. All the samples were used for the training of the model, which resulted in their correct classification. At Qvidja farm 28 samples were used for model development (22 for training and 6 for validation), and the resulted model allowed the correct classification of 83.3% of the samples used for validation. In this way, it was possible to confirm the statistical influence of the sampling site on the VOCs composition in gas phase and aerosol particle samples. The detailed analysis of the LDA models, including the taxonomical groups, responsible for the differentiation between sampling sites, can be found in Table S14.

4. Conclusions

The use of MAS systems, integrated with an aerial drone for the quantitative analysis of VOCs in gas phase and aerosol particles was demonstrated. Different sampling systems, carried by drone, were technically further developed to improve their versatility and robustness. In addition, the detailed quality control and assurance carried out for the different MAS systems in the drone allowed the evaluation of the reliability of the results. Several parameters were determined in this study, including the equilibrium sampling time for SPME Arrow system and breakthrough volume for ITEX that depended on the analyte under study. Variations under 15% were observed for the packing of ITEX units and coating reproducibility for SPME Arrow units. The storage time did not have any significant effect on the sample composition up to 48 h at −20 °C.

In addition, the effect of the drone propellers on the active ITEX and passive SPME Arrow systems was evaluated without any significant influence on ITEX with recoveries close to 100% in all the cases. However, some important findings were made for SPME Arrow samplers, such as the importance of the SPME Arrow position in the drone platform to minimize the effect of propellers on the results. The SPME Arrow when located close and under the body of the drone gave the best, over 95% recoveries.

Classification of compounds into taxonomical groups and the development of their PLSR equations allowed the quantitation of the studied compounds and the semi-quantitation of those belonging to the same taxonomical group. The prediction error for compounds not used in the development of the equations was in all the cases under 27%.

The MAS-drone system was used in two different sampling sites, one at the SMEAR II station and another in Qvidja farm in summer 2019. The simultaneous use of active ITEX and passive SPME Arrow samplers, together with developed individual PLSR equations enabled the

clarification of the VOC composition in different gas and aerosol phase samples.

Clear differences between both sites in terms of total number of compounds and VOC composition seen can be explained by the very different meteorological and environmental conditions observed at the sites. In addition, due to practical reasons sampling heights were not exactly the same in both sites. In the case of the SMEAR II station, the taxonomical groups responsible for the differences in the samples were related to compounds emitted by the trees and their potential oxidation products. However, in the case of Qvidja farm, most of these differences were caused by organonitrogen compounds. Especially, clear differences were observed for dimethylamine in all the studied cases.

Overall, our study demonstrates a relatively comprehensive study of the MAS-drone system for quantitative/semi-quantitative analysis of VOCs in air and aerosol particles. The system can be further developed for on-site air monitoring by using a portable GC-MS system or by well-constructed facilities available at the SMEAR II station.

Credit author statement

Hangzhen Lan: Investigation, Methodology, Validation, Visualization **Jose Ruiz-Jimenez**: Methodology, Visualization, Writing – original draft, Formal analysis **Yevgeny Leleev**: Investigation, Validation **Giorgia Demaria**: Investigation **Matti Jussila**: Methodology, Software. **Kari Hartonen**: Conceptualization, Reviewing and Editing **Marja-Liisa Riekkola**: Conceptualization, Supervision, Reviewing and Editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131024.

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